LIQUID PHASE GROWTH METHODS AND

LIQUID PHASE GROWTH APPARATUS

BACKGROUND OF THE INVENTION

5   Field of the Invention

The present invention relates to liquid phase growth methods and liquid phase growth apparatus and, more particularly, is suitably applicable to liquid phase growth methods and liquid phase growth apparatus

10   of an immersion type in which a substrate of wafer size is held by a jig and immersed into a solution containing a growth material.

Related Background Art

Global environments are becoming worse because of

15   emission of earth-warming gases such as carbon dioxide, nitrogen oxides, etc. from combustion of petroleum in thermal power generation, combustion of gasoline in automotive engines, and so on. In addition, there is future concern about a drain of crude oil and attention

20   is thus being drawn toward power generation with solar cells as clean energy sources.

Since thin-film crystal silicon (Si) solar cells have a thin power-generating layer and are made using a small amount of the source material of Si, there is a

25   perspective of cost reduction of the thin-film crystal Si solar cells. Since the power-generating layer is made of crystal Si, higher conversion efficiency and

less deterioration can be expected as compared with
solar cells of amorphous Si and others. Further, since
the thin-film crystal Si solar cells can be bent to
some extent, they can be used in a bonded state to

5   curved surfaces of automotive bodies, household
electrical appliances, roof tiles, and so on.

       For substantiating the thin-film crystal Si solar
cells, Japanese Patent Application Laid-Open No. 8-
213645 discloses separation of thin films of

10   monocrystalline Si, making use of epitaxial layers on a
porous Si layer. Fig. 16 is a cross-sectional view
showing a method of forming a thin-film Si solar cell,
described in Japanese Patent Application Laid-Open No.
8-213645. In the figure, numeral 101 designates an Si

15   wafer, 102 a porous Si layer, 103 a p^+ type Si layer,
104 a p^- type Si layer, 105 an n^+ type Si layer, 106 a
protective film, 109 and 111 adhesive layers, and 110
and 112 jigs. In the process of producing the solar
cell of Fig. 16, the porous Si layer 102 is made by

20   anodization over the surface of Si wafer 101. After
that, the p^+ type Si layer 103 is epitaxially grown on
the porous Si layer 102, and the p^- type Si layer 104
and n^+ type Si layer 105 are further grown thereon.
Then, the protective film 106 is formed thereon. The

25   adhesive layers 111, 109 are then laid over the
protective film 106 and over the Si wafer 101,
respectively, to be bonded to the jigs 112, 110.

Thereafter, pulling forces P are exerted on the respective jigs 110, 112 to separate the Si wafer 101 from the epitaxially grown Si layers (103, 104, 105) across the porous Si layer 102. Then, the solar cell

5 is formed in the epitaxially grown Si layers (103, 104, 105), while the Si wafer 101 is again subjected to similar steps, thereby reducing the cost.

Japanese Patent Application Laid-Open No. 5-283722 discloses growth of epitaxial Si layers on the porous

10 Si layer by the liquid phase growth method. An Sn melt is used as a solvent, and Si is preliminarily dissolved into the Sn melt to saturate therein, prior to the growth. Then, the melt is slowly cooled, and at a certain level of supersaturation a porous surface of a

15 wafer is dipped into the Sn melt to grow an epitaxial Si layer on the porous surface.

Japanese Patent Application Laid-Open No. 5-17284 discloses an immersion type liquid phase growth apparatus of compound semiconductor and a holding jig.

20 Fig. 17 is a cross-sectional view of this liquid phase growth apparatus. In the figure, numeral 81 designates a wafer holder, 82 a wafer, 83 a crucible, 84 a solution, 85 a quartz reactor tube, 886 a gas introducing tube, 887 a gas exhaust tube, 88 a heater,

25 and 89 a dummy wafer. In this immersion type liquid phase growth apparatus, the wafer holder 81 holding the wafer 82 and dummy wafer 89 is moved down (in the

direction A), the wafer 82 is immersed into the
solution 84 in which a growth material is dissolved.
The solution 84 is retained in the crucible 83 and the
crucible 83 is placed in the quartz reactor tube 85

5   which maintains the interior in an atmospheric (or
ambient) gas (reducing gas or inert gas) by means of
the gas introducing tube 86 and gas exhaust tube 87.
The heater 88 is provided for control of temperature of
the system. The temperature of the solution 84 is

10   lowered by decreasing the temperature of the heater 88,
whereby the growth material is precipitated from the
solution 84 onto the wafer 82 to grow in liquid phase.
The immersion type liquid phase growth apparatus can be
constructed in smaller size as the growth apparatus for

15   liquid phase growth on wafers of the same size than the
liquid phase growth apparatus of the slide boat type
and the liquid injection type. The immersion type
liquid phase growth apparatus is also convenient for
mass production, because a lot of wafers can be set on

20   the holder.

Japanese Patent Application Laid-Open No. 57-76821
also discloses an immersion type liquid phase growth
method. Fig. 18A is a perspective view of a wafer
holder disclosed in Japanese Patent Application Laid-

25   Open No. 57-76821. Numeral 123 designates an arm, 124
an umbrella-like plate, 125 wafers, 126 a through hole,
and 122 a cylindrical member. This wafer holder can be

loaded with six substrates on the umbrella-like plate
124. Fig. 18B is a plan view of this wafer holder.
Fig. 18C shows a crucible 128 into which the wafer
holder shown in Figs. 18A and 18B is immersed, and a
solution 129 is filled in the crucible 128. A heater
130 is placed around the crucible 128 and an auxiliary
heater 131 projecting upright is located in the center
and in the lower part of the crucible 128. Namely, the
crucible 128 is recessed toward the interior around the
auxiliary heater 131 and the auxiliary heater 131 is
placed inside the recess. Since this auxiliary heater
131 prevents the central part of the solution 129 from
becoming lower in temperature than the peripheral part,
the solution 129 is wholly kept at even growth
temperature. It is disclosed that this arrangement can
thus implement the uniform liquid phase growth.

In the case of the immersion type liquid phase
growth apparatus disclosed in Japanese Patent
Application Laid-Open No. 5-17284 described referring
to Fig. 17, when the wafer size is large for liquid
phase growth over a large area, a deposited film
becomes thick in the peripheral part of the wafer but
thin in the central part. Fig. 19 is a cross-sectional
view showing the growth of the deposited film. In the
figure, numeral 82 denotes a wafer and 90 an epitaxial
film deposited on the wafer 82. As illustrated, for
the large wafer size, the deposited film 90 becomes

thin in the central part of the wafer but thick in the peripheral part. This phenomenon becomes noticeable, particularly, when the wafer size is not less than five inches. A conceivable reason for it is that the

5   outside part of the solution 84 is close enough to the atmospheric gas to reduce the temperature of the outside part of the solution according to the cooling of the system whereas the central part of the solution 84 is far from the atmospheric gas and is thus cooled

10   with a lag behind the temperature reduction of the outside part. Namely, a temperature change is less since a growth start in the central part of the wafer than in the peripheral part. For this reason, a deposition amount of the deposited film 90 is

15   considered to be smaller in the central part of the wafer than in the peripheral part.

This is also the case in the liquid phase growth method disclosed in Japanese Patent Application Laid-Open No. 57-76821, and the temperature is less unlikely

20   to be reduced in the central part of the crucible than in the peripheral part, because there is no mechanism of intentionally cooling the solution in the crucible. For this reason, a precipitation amount of the solute is less in the central part of the crucible, so that

25   the thickness of the deposited film is also thinner on the wafer near the central part of the crucible.

When the deposited film on the wafer has

dispersion of thickness as described above, there is a possibility of contact failure, for example, when electrodes are attached to the surface of the deposited film in production of solar cell. In addition, since the thickness of the deposited film has to be determined in the thin part for sufficient absorption of light, the thick part becomes over specifications and thus the material of the deposited film is wasted. Besides, where the deposited film is thick, the peripheral part of the film is too thick for photocarriers to reach the electrodes because of the too large thickness, which degrades light conversion efficiency. For this reason, when the solar cell is made on the wafer, the deposited film is preferably made as uniform as possible. In the case of semiconductor devices other than the solar cells, the dispersion of thickness of the deposited film will require different design between in the central part and in the peripheral part of the wafer, which will increase the number of steps and, in turn, increase the production cost.

SUMMARY OF THE INVENTION

An object of the present invention is to solve the above problems separately or all together. Specifically, an object of the invention is to form a deposited film having a uniform thickness entirely over

the substrate by the liquid phase growth on the substrate such as the wafer or the like.

In order to solve the aforementioned problems, the inventors conducted elaborate research and accomplished the following invention as a result.

For achieving the above object, an aspect of the present invention is a liquid phase growth method comprising the steps of:

immersing a substrate in a crucible that stores a solvent having a growth material dissolved therein; and

cooling the solvent from an interior thereof.

The solvent is preferably cooled from a central part thereof.

It is preferable to implement the cooling step by letting a medium flow through a tube immersed in the crucible; by letting a medium flow through a hole formed in a jig for holding the substrate; or by letting a medium flow through a hole formed in the crucible.

Another aspect of the present invention is a liquid phase growth apparatus comprising:

a crucible for storing a solvent having a growth material dissolved therein;

a wafer cassette for holding a substrate to be immersed in the solvent; and

a cooling section for cooling the solvent from an interior thereof.

The cooling section is preferably a tube which is immersed in the crucible and through which a medium is made to flow, a hole which is formed inside a wafer cassette and through which a medium is made to flow, or a hole which is formed in the crucible and through which a medium is made to flow.

The foregoing medium is, for example, a gas. The gas is preferably hydrogen or nitrogen gas as an atmospheric gas.

A liquid phase growth bath for formation of a p^- type Si layer may be used as the crucible and, subsequent thereto, a liquid phase growth bath for formation of an n^+ type Si layer may be used as the crucible.

The growth material is, for example, Si, Ge, or GaAs.

The solvent is, for example, a melt of In or Sn.

The wafer cassette is preferably rotatable about its own axis.

The wafer cassette is preferably revolvable about an axis different from its own axis.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A is a longitudinal cross-sectional view of a wafer cassette and a crucible of a liquid phase growth apparatus of Embodiment 1 taken along line 1A-1A of Fig. 1B, and Fig. 1B is a horizontal cross-sectional

view of the wafer cassette and the crucible of the liquid phase growth apparatus of Embodiment 1 taken along line 1B-1B of Fig. 1A;

Fig. 2 is a longitudinal cross-sectional view of the liquid phase growth apparatus of Embodiment 1;

Figs. 3A, 3B, 3C, 3D, and 3E are a flowchart consisting of cross-sectional views showing production steps of a solar cell;

Figs. 4A, 4B, 4C, and 4D are a flowchart consisting of cross-sectional views showing production steps of a solar cell;

Figs. 5A and 5B are longitudinal cross-sectional views of respective anodization systems;

Fig. 6 is a perspective view of a solar-battery unit cell;

Fig. 7A is a longitudinal cross-sectional view of wafer cassettes and a crucible in Embodiment 2 taken along line 7A-7A of Fig. 7B, and Fig. 7B is a horizontal cross-sectional view of the wafer cassettes and the crucible in Embodiment 2 taken along line 7B-7B of Fig. 7A;

Fig. 8 is a longitudinal cross-sectional view of the liquid phase growth apparatus of Embodiment 2;

Fig. 9A is a longitudinal cross-sectional view of a wafer cassette and a crucible in Embodiment 3 taken along line 9A-9A of Fig. 9B, and Fig. 9B is a horizontal cross-sectional view of the wafer cassette

and the crucible in Embodiment 3 taken along line 9B-9B of Fig. 9A;

Fig. 10A is a plan view of a wafer in Embodiment 3, Fig. 10B is a plan view of an array of solar-battery unit cells arranged, Fig. 10C is a plan view of another wafer, and Fig. 10D is a plan view of an array of solar-battery unit cells arranged;

Fig. 11 is a longitudinal cross-sectional view of a wafer cassette in Embodiment 4;

Fig. 12 is an oblique cross-sectional view of the wafer cassette in Embodiment 4 taken along line 12-12 of Fig. 11;

Fig. 13 is a plan view of a liquid phase growth system in Embodiment 4;

Fig. 14 is a longitudinal cross-sectional view of the liquid phase growth system of Embodiment 4 taken along line 14-14 of Fig. 13;

Fig. 15 is a time chart showing a sequence of liquid phase growth in Embodiment 4;

Fig. 16 is a longitudinal cross-sectional view showing a typical solar cell production step;

Fig. 17 is a longitudinal cross-sectional view of a typical liquid phase growth apparatus;

Figs. 18A, 18B, and 18C are schematic views showing a typical liquid phase growth apparatus; and

Fig. 19 is a cross-sectional view of a deposited layer by a typical liquid phase growth method.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Embodiments of the present invention will be described below in detail with reference to the drawings. Four embodiments will be described below, but it is noted that the present invention is not limited to the embodiments but combinations thereof are also included in the scope of the invention.

(Embodiment 1)

In Embodiment 1, a main shaft at the center of a wafer cassette supporting Si wafers is of hollow structure. The atmospheric gas is made to flow through this hollow structure (vent hole), thereby enhancing the effect of cooling the central part of the liquid. Figs. 1A and 1B are a longitudinal cross-sectional view and a horizontal cross-sectional view, respectively, of the wafer cassette of Embodiment 1. Fig. 1A is a cross-sectional view taken along a line 1A-1A of Fig. 1B, and Fig. 1B a cross-sectional view taken along a line 1B-1B of Fig. 1A. In the figures, numeral 1 designates a crucible, 2 a main shaft, 3 a vent hole, 4 a solution stored in the crucible 1, 5 wafer support pins, 6 Si wafers, 7 shafts of rotation, 8 support-pin-fixing disks, and 11 a rotation-shaft-supporting disk. The crucible 1, main shaft 2, wafer support pins 5, rotation shafts 7, support-pin-fixing disks 8, and rotation-shaft-supporting disk 11 are preferably made of quartz so as to resist temperatures of approximately

1000°C.

Fig. 2 is a longitudinal cross-sectional view of the liquid phase growth apparatus including a heater 10, a driving system 22, and the wafer cassette 15 of Figs. 1A and 1B. The crucible 1 and wafer cassette 15 are set in the quartz reactor tube 14. The heater 10 is set outside the quartz reactor 14 and is composed of three parts top, middle, and bottom. The central part is placed around the crucible 1 to heat the crucible 1. The heater also covers a range approximately equal to the height of the crucible 1 above the crucible 1. This is for cleaning surfaces of the Si wafers 6 by hydrogen annealing at the temperature of about 1040°C before the wafer cassette 15 is immersed into the crucible 1.

The driving system 22 will be described below. In Fig. 2, numeral 13 denotes a motor for the shaft of revolution, 12 motors for the rotation shafts, 16 rotation-shaft supports, 17 a main-shaft support, 18 an upper rotation-shaft-supporting disk, 19 and 20 couplings, 21 a wafer cassette support system, and 23 lead wires for supplying power to the revolution-shaft motor 13 and to the rotation-shaft motors 12. The rotation-shaft supports 16, main-shaft support 17, upper rotation-shaft-supporting disk 18, and entire support are made of stainless steel. The main-shaft support 17 is coupled to the quartz main shaft 2 at the

coupling 20 with bolts and nuts or the like. The
rotation shafts 7 are also coupled similarly to the
rotation-shaft supports 16 at the couplings 19.
Numeral 86 is a gas introducing tube for introducing
5   the atmospheric gas of hydrogen, nitrogen, or the like
into the quartz reactor 14.

The wafer cassette support system 21 is continuous
from the outer frame and supports the driving system
22, the wafer cassette 15, and so on. The revolution-
10   shaft motor 13 rotates the main shaft 2 serving as an
axis of revolution of the wafer cassette 15 through the
main shaft support 17. The lead wires are routed
through the main shaft support 17, so that the power is
supplied to the rotation-shaft motors 12 through the
15   wires. Ring electrodes are placed in the revolution-
shaft motor 13 so that electrical conduction is
maintained between the lead wires 23 and the lead wires
in the main shaft support even during revolution of the
main shaft support 17.

20   The following will describe an example of
production of a peeling type solar cell, using the
liquid phase growth apparatus of Embodiment 1. Figs.
3A to 3E and Figs. 4A to 4D are cross-sectional views
showing production steps of the solar cell of this
25   structure, and Fig. 6 is a perspective view of the
complete solar cell.

First, the monocrystalline Si wafer 6 is prepared

as shown in Fig. 3A. Then, a porous Si layer 27 is
formed in the thickness (1 to 30 µm) on the surface of
the Si wafer 6 by anodization, as shown in Fig. 3B.
The thickness of the Si wafer 6 is about 600 µm and the

5   porous Si layer 27 about 1 to 30 µm. Therefore, only
an extreme surface region of the Si wafer 6 is changed
into the porous Si layer 27. The major part of the Si
wafer 6 remains as non-porous Si layer 28.

Figs. 5A and 5B are cross-sectional views of

10   respective systems for treating (or anodizing) the Si
wafer 6 with a hydrofluoric acid base etchant. In the
figures, numeral 6 denotes the Si wafer, 541 the
hydrofluoric acid base etchant, 542 and 543 metal
electrodes, and 544 an O-ring. The Si wafer 6 to be

15   treated is desirably of the p-type, but may be of the
n-type if the resistance is low. It is also possible
to make even the n-type wafer porous if it is in a
hole-generated state under irradiation with light.
When the system is arranged so that a voltage is placed

20   between the two electrodes with the lower metal
electrode 542 being positive and the upper metal
electrode 543 being negative and so that an electric
field caused by this voltage is applied normally to the
surface of the Si wafer 6 as shown in Fig. 5A, the

25   upper surface of the Si wafer 6 is made porous. When
the system is arranged so that the Si wafer 6 is placed
between the two electrodes and so that the voltage is

applied with the left metal electrode 542 being
positive and the right metal electrode 543 being
negative as shown in Fig. 5B, the right surface or
negative-electrode-side surface of the Si wafer 6 is
5 made porous. The hydrofluoric acid base etchant 541
is, for example, concentrated hydrofluoric acid (e.g.,
49% HF). The metal electrodes 542, 543 are, for
example, Pt, Au, or the like. During the anodization
bubbles evolve from the Si wafer 6. In order to
10 eliminate the bubbles efficiently, alcohol is sometimes
added as a surfactant. The alcohol is desirably either
of methanol, ethanol, propanol, isopropanol, and so on.
An agitator may also be used instead of the surfactant
so as to perform the anodization while agitating the
15 solution. The thickness of the surface to be made
porous is desirably 0.1 to 30 μm and more desirably 1
to 10 μm.

In the anodization step, in order to facilitate
the later work in the separation step, the electric
20 current from the metal electrode 542 to the metal
electrode 543 is altered during the anodization. For
example, a small electric current is allowed to flow in
the first half of anodization to make the extreme
surface layer of the Si wafer 6 porous, and a large
25 electric current is allowed to flow in the second half
of anodization to make porous the region near the
interface between the non-porous Si layer 28 and the

porous Si layer 27. In this case, the surface layer in
the porous Si layer 27 is made in structure of small
pores facilitating the later epitaxial growth, while
the layer on the non-porous Si layer 28 side of the
5   porous Si layer 27 is made in structure of large pores
facilitating the separation. This structure results in
facilitating execution of the later epitaxial growth
step and the separation step. It is a matter of course
that the anodization may also be carried out at a fixed
10   electric current, for simplicity of steps.

     Next, as shown in Fig. 3C, a p$^-$ type Si layer 25 of
an epitaxial layer (single crystal) is grown on the
porous Si layer 27 by liquid phase growth. The
thickness of this layer is 20 to 50 μm. In the case of
15   Embodiment 1, this epitaxial layer is the deposited
film of the present invention. This step is carried
out by the liquid phase growth apparatus and method of
the present invention described referring to Figs. 1A
and 1B and Fig. 2. The details will be described
20   below.

     First, to-be-dissolved Si wafers as washed with
dilute hydrofluoric acid or the like are set on the
wafer cassette 15. The wafer support pins 5 are
provided with slots for Si wafers to be inserted
25   thereinto. The Si wafers are slid into the slots to be
supported thereon. The slots of the wafer support pins
5 are formed so as to support the Si wafers obliquely,

in order to prevent the solution 4 from remaining on
the Si wafers when the Si wafers 6 are lifted up from
the solution 4.

Next, the wafer cassette 5 is attached to the
driving system 22 through the couplings 19, 20, as
shown in Fig. 2. At this time, it is preferable to
preset the coupling 20 of the main shaft 2 in a regular
coupling state and uncouple only the couplings 19 to
allow insertion and extraction of the wafer cassette
15. The wafer cassette 15 is incorporated into the
liquid phase growth apparatus in this way, and the
wafer cassette 15 is placed immediately above the
solvent, as shown in Fig. 2. Then, the heater 10 is
energized and annealing is carried out at 1040°C for
about ten minutes to clean the surfaces of Si wafers 6.
This annealing is carried out in a hydrogen atmosphere.
At this time, it is desirable to rotate the Si wafers
by means of the revolution motor 13 and rotation motors
12.

After that, the energization state of the heater
10 is adjusted to control the solvent in the crucible 1
to the temperature of about 960°C, and then the wafer
cassette 15 and the driving system 22 are moved down by
the vertical motion mechanism to immerse the Si wafers
into the solvent. The Si wafers are kept in the
immersed state for about one hour. During this period
Si is dissolved from the Si wafers into the solvent.

Then, the wafer cassette 15 is lifted up from the solution 4 and the wafer cassette 15 is taken out of the liquid phase growth apparatus to complete the dissolution of Si into the solvent. The solvent
5   containing Si is prepared in this way.

In the next place, Si wafers 6 with the porous Si layer 27 on the surface, also cleaned with dilute hydrofluoric acid or the like, are set on another wafer cassette 15. Then, the wafers 6 are annealed in a
10   hydrogen atmosphere as the dissolving wafers were. Thereafter, the energization state of the heater 10 is adjusted to control the temperature to 950°C. At this stage, Si goes into a supersaturated state in the solution 4 containing it. Then, the wafer cassette 15
15   and the driving system 22 are moved down by the vertical motion mechanism to immerse the Si wafers 6 into the solution 4. After that, the energization state of the heater 10 is adjusted to control the solution 4 gradually down to about 900°C, whereupon a
20   film of Si is deposited from the solution 4 onto the Si wafers 6. Then, the wafer cassette 15 is lifted up from the solution 4 and is taken out of the liquid phase growth apparatus to complete the liquid phase growth.

25   In the liquid phase growth of Embodiment 1, it is normally desirable to rotate the Si wafers about their own axes and revolve the Si wafers about the principal

axis by the rotation-shaft motors 12 and the
revolution-shaft motor 13. However, even the interior
of the solution 4 varies following the temperature in
the atmosphere in the quartz reactor 14 through the

5   vent hole 3. For this reason, uniformity of thickness
of the epitaxial layer by the liquid phase growth can
be ensured even without the rotation and revolution of
the Si wafers in particular. Accordingly, it is
possible to employ either of the rotation and

10   revolution or neither of the rotation and revolution,
particularly, during the growth.

     After completion of the liquid phase growth of the
p$^-$ type Si layer 25 by the liquid phase growth method,
the surface part of the p$^-$ type Si layer 25 is changed

15   into an n$^+$ type Si layer 24 by diffusion of an impurity,
as shown in Fig. 3D. Then, surface electrodes 31 are
formed by a method of printing or the like on the n$^+$
type Si layer 24, as shown in Fig. 3E. The surface
electrodes 31 have the structure like comb teeth as

20   shown in Fig. 6 of a perspective view. Then, an
antireflection coating of TiO (titanium oxide), MgF
(magnesium fluoride), SiN (silicon nitride), or the
like is formed on those regions which are not covered
by the surface electrodes 31 of the n$^+$ type Si layer 24

25   by a method of sputtering or the like, and a glass
substrate 33 is bonded thereonto with an adhesive, as
shown in Fig. 4A.

After that, pulling forces are exerted between the glass substrate 33 and the non-porous Si layer 28 to separate the part to become the solar cell, from the non-porous Si layer 28 at the part of the porous Si

5   layer 27. The non-porous Si layer 28 thus separated is then treated with an alkali etchant to remove the residue of porous Si remaining on the surface, and it is again used as Si wafer 6 in the steps from Fig. 3A. The part to become the solar cell as separated in Fig.

10   4B is also treated with the alkali etchant to remove the residue of porous Si layer 27 and obtain the residueless structure as shown in Fig. 4C. After that, as shown in Fig. 4D, a back electrode 32 of stainless steel or Al sheet or the like is bonded to the back

15   surface of the p⁻ type Si layer 25 with an electroconductive adhesive, thereby completing the unit cell for a solar cell of Fig. 6. The bonding of the back electrode 32 to the p⁻ type Si layer 25 may also be implemented by thermal bonding.

20   When the liquid phase growth of the immersion type is carried out using the liquid phase growth apparatus of Embodiment 1, the central part of the solution can also be cooled in accordance with the temperature control of the heater, whereby the deposited film can

25   be grown with less thickness dispersion. Further, a lot of Si wafers can be set on the wafer cassette, which is suitable for mass production. Embodiment 1

was described above as the example in which the porous
Si layer was formed on the Si wafer and in which the
monocrystalline Si layer was epitaxially grown thereon,
but it is noted that the Si wafer may be replaced by a
5   Ge or GaAs wafer and that Ge, GaAs, or the like may be
grown on the porous Si layer obtained by anodization of
the Si wafer. The embodiment was the example of
production of the solar cell, but the present
embodiment may also be applied to production of an
10   epitaxial wafer, an SOI (Silicon on Insulator)
substrate, and so on.
(Embodiment 2)

     In Embodiment 2, the central part of the crucible
is of hollow structure. The atmospheric gas is made to
15   flow through this hollow structure (vent hole), which
enhances the cooling effect of the central part of the
solution. In Embodiment 2, four wafer cassettes 15 are
immersed into one crucible. Figs. 7A and 7B are a
longitudinal cross-sectional view and a horizontal
20   cross-sectional view, respectively, of the wafer
cassettes and the crucible in Embodiment 2. The
reference numerals of the components are the same as
those in the foregoing figures. Fig. 8 is a cross-
sectional view of the apparatus in a state in which the
25   wafer cassettes are lifted from the crucible 1.
Numeral 86 designates a gas introducing tube, and 87 a
gas exhaust tube. In this liquid phase growth

apparatus, each wafer cassette is rotated only about
its own axis by the rotation-shaft motor 12, and the
revolution mechanism as in Embodiment 1 is not
provided, which simplifies the structure. As shown in
5   Figs. 7A and 7B and Fig. 8, the crucible 1 of
Embodiment 2 is provided with the vent hole 3 in the
central part to allow the flow of the atmospheric gas
9, so that the central part of the solution 4 can also
be cooled as the peripheral part can. The shapes of
10   the gas introducing tube and gas exhaust tube are
properly modified in order to secure the flow of the
atmospheric gas 9.

(Embodiment 3)

     In Embodiment 3, the central part of the crucible
15   storing the solution is also of hollow structure, as in
Embodiment 2. The atmospheric gas is also made to flow
through the hollow structure (vent hole), which
enhances the cooling effect of the central part of the
solution. However, there is only one wafer cassette
20   provided, and each Si wafer has a hole in the central
part. Figs. 9A and 9B are a longitudinal cross-
sectional view and a horizontal cross-sectional view,
respectively, of the wafer cassette and crucible in
Embodiment 3. Reference numerals of the components are
25   the same as those in the foregoing figures. The
sectional view of Fig. 9A is a cross section taken
along a line 9A-9A in the sectional view of Fig. 9B.

The sectional view of Fig. 9B is a cross section taken
along a line 9B-9B in the sectional view of Fig. 9A.
In Embodiment 3 each Si wafer 6 is hexagonal and a
hexagonal hole is bored in the central part thereof.

5   While the Si wafers 6 are immersed into the crucible 6
filled with the solution 4, the vent hole 3 of the
crucible 1 passes through the holes in the center of
the Si wafers. The hexagonal Si wafers are Si wafers
with the surface of (111) plane, and it is desirable to

10   form the wafers into the hexagonal shape by making use
of their cleavage.

In the liquid phase growth of Embodiment 3, since
the atmospheric gas can be fed to near the solution in
the central part of the Si wafers, the temperature of

15   the solution 4 is uniformly lowered in the central part
and in the peripheral part of each Si wafer, whereby a
film can be liquid-phase-grown in uniform thickness
across the entire wafer. Each Si wafer 6 is supported
by three wafer support pins 5 connected to the support

20   pin fixing disk 8 and is rotated thereby, which permits
the liquid phase growth to be done with better
uniformity. When the liquid phase growth of Embodiment
3 is applied to the production steps of solar cell
described in Embodiment 1, approximately hundred thin-

25   film monocrystalline solar-battery unit cells are
obtained from a single Si wafer.

A thin film of single crystal grown and peeled in

Embodiment 3 is cut along dotted lines of Fig. 10A to obtain solar-battery unit cells 37. Complete solar-battery unit cells 37 are arranged as shown in Fig. 10B to obtain a solar cell module 38 at a high fill factor.

5 In Embodiment 3, it is also possible to use Si wafers with a square circumference and with a square hole in the center, as shown in Fig. 10C, and to carry out the liquid phase growth and the cell formation of solar cells according to similar methods, thereby forming

10 unit cells 39. In this case, the unit cells 39 are arranged as shown in Fig. 10D to obtain a solar cell module 40 at a high fill factor. The modules of Figs. 10B and 10D have the shapes like geometrical patterns, which add the effect of enhancing diversity of design,

15 for example, where the solar cells are mounted on roofs of houses.

(Embodiment 4)

In Embodiment 4, the wafer cassette is provided with a vent hole. Fig. 11 and Fig. 12 are longitudinal

20 and oblique cross-sectional views, respectively, of the wafer cassette 68 of Embodiment 4. The sectional view of Fig. 12 is a cross section taken along a line 12-12 of Fig. 11, viewed from obliquely above. In the figures, numeral 41 designates support columns, 44

25 covers (wafer covers), 45 seatings (wafer backing seatings), and 50 a column-supporting disk, all of which are made of quartz so as to resist the

temperature of about 1000°C. In Embodiment 4 the wafer cassette has the wafer backing seatings 45 for holding Si wafers 6 thereon, and the Si wafers 6 are held on the back and front surfaces of the wafer backing seatings 45. The columns 41 supporting each of the wafer backing seatings 45, and the wafer backing seatings 45 themselves are made of quartz in integral structure. The column-supporting disk 50 is made of quartz in integral structure with the columns 41 to support the columns 41. Numeral 6 denotes the Si wafers, each of which has an orientation flat at the position of 49 in Fig. 12. Each Si wafer is embedded in a counterbore (depression) of the wafer backing seating 45 and is held by means of the wafer cover 44.

The wafer backing seatings 45 have the diameter approximately 0.1 to 0.5 mm larger than that of the Si wafers 6, and each seating 45 is provided with a counterbore (depression) matching the shape of the orientation flat part 49 of the Si wafer 6. Each Si wafer 6 is embedded in the counterbore. Therefore, the wafer backing seatings 45 serve as holding plates for holding the Si wafers 6. The diameter of the wafer covers 44 is 1 to 5 mm smaller than the size of the Si wafers 6, as shown in Fig. 12, so as to be able to support the Si wafers 6 only in the peripheral part of each Si wafer 6. Each wafer cover 44 is provided with an aperture 47 corresponding to the shape of the

orientation flat part 49. Grooves 48 are formed at
joints between the columns 41 and the wafer backing
seatings 45, as shown in Fig. 11. The wafer covers 44
are fitted into the grooves 48 whereby the wafer covers

5   44 are fixed. For mounting or dismounting a wafer
cover 44, the wafer cover 44 is rotated in the grooves
48 before notches 46 shown in Fig. 12 are aligned with
the columns 41. This structure for fixing the Si wafer
6 is also common to the portions for supporting the

10   other Si wafers 6.

The vent hole 3 is routed inside the columns 41
and the wafer backing seatings 45 of this wafer
cassette. The atmospheric gas is made to flow through
this vent hole 3 up to the central part of the solution

15   to cool the central part of the solution positively.
For this reason, the wafers are cooled at an equal
temperature reduction rate in the central part and in
the edge part during the liquid phase growth, so as to
implement the growth in uniform thickness. The upper

20   end of the vent hole 3 reaches the top of the column-
supporting disk 50 and serves as an exit/entrance for
the atmospheric gas. In Embodiment 4, a gas
introducing tube may be placed near this exit/entrance
to positively supply the atmospheric gas into the vent

25   hole 3.

In Embodiment 4, a liquid phase growth apparatus
of a dual bath type may also be used. Fig. 13 is a

plan view from the top of the liquid phase growth
apparatus of the dual bath type. In the figure,
numeral 51 designates a loading chamber (L/C), 52 a
hydrogen annealing chamber, 54 a growth chamber of p⁻

5   type Si layer 25, 55 a growth chamber of n⁺ type Si
layer 24, 56 an unloading chamber (UL/C), and 63 a core
in which a conveying system of wafer cassette 68 is
located. Numerals 58 and 59 represent transport
chambers for supplying the Si source to the respective

10   growth chambers of the p⁻ type Si layer and the n⁺ type
Si layer, and numerals 61 and 62 Si source stockers for
supply of the Si source to the respective growth
chambers of the p⁻ type Si layer and the n⁺ type Si
layer.

15   For the liquid phase growth, the wafer cassette 68
provided with the vent hole 3 and loaded with Si wafers
6 is carried into the loading chamber (L/C) 51. Then,
the wafer cassette 68 in the loading chamber (L/C) 51
is moved into the hydrogen annealing chamber 52 by the

20   conveying system placed in the core 63, and the
hydrogen annealing is carried out therein. Thereafter,
the wafer cassette 68 is transferred successively to
the growth chamber 54 of p⁻ type Si layer 25 and to the
growth chamber 55 of n⁺ type Si layer 24 to form the p⁻

25   type Si layer and the n⁺ type Si layer in order on the
Si wafers 6.

        Fig. 14 is a cross-sectional view of Fig. 13 taken

along a cutting surface 14-14. In the figure, numeral
64 designates a solution, 65 a heater, 66 a crucible,
68 the wafer cassette of the present embodiment, 69 a
vertical conveying system, 70 horizontal conveying

5   systems, 86 a dissolving wafer cassette, 87 dissolving
wafers, and 38 a coupling. The components denoted by
the reference symbols described previously are the same
as the aforementioned components and thus the
description thereof is omitted herein.

10   The loading chamber 51 is usually isolated from
the core 63 and the external atmosphere by gate valves
67. When the right gate valve 67 of the loading
chamber 51 is opened, the wafer cassette 68 can be
moved into the loading chamber 51. When the left gate

15   valve of the loading chamber 51 is opened, the wafer
cassette 68 can be moved into the growth chamber 54 of
p⁻ type Si layer by means of the horizontal conveying
system 70 in the core 63.

The Si source supply chamber 61 is constructed so

20   that the dissolving wafer cassette 86 can be moved into
or out of the chamber by opening the left gate valve
67. When the right gate valve is opened, the
dissolving wafer cassette 86 can be moved into the
growth chamber 54 of p⁻ type Si layer by means of the

25   horizontal conveying system 70 in the transport chamber
58. The growth chamber 54 of p⁻ type Si layer has the
vertical conveying system 69 for vertically moving the

wafer cassette 68 and the dissolving wafer cassette 86.
The vertical conveying system 69 can immerse the wafer
cassette 68 and the dissolving substrate cassette 86
into the solvent 64 (also called a melt) stored in the

5   crucible 66. At the coupling 38 the quartz wafer
cassette 68 is coupled to the vertical conveying system
69 of stainless steel. This coupling method is
desirably a locking system. The heater 65 heats the
melt to a high temperature to keep the melt in a liquid

10   state. The growth chamber 55 of n⁺ type Si layer, the
transport chamber 59, and the Si source supply chamber
62 are also of the same sectional structure as in Fig.
14. With the wafer cassette 68, the back and side
surfaces of the Si wafers 6 are kept from touching the

15   solution 64 so that a thin film is grown over only the
exposed front surfaces and so that no thin film is
grown on the back and the side surfaces of Si wafers 6.
On the other hand, the dissolving wafer cassette 86 has
the structure in which the front surface, back surface,

20   and side surface all touch the solvent so as to
dissolve as large an amount of Si from each wafer as
possible. For growth of a thin film, it is desirable
to rotate the wafer cassette 68 by the vertical
conveying system 69.

25   Fig. 15 is a time chart showing the sequence of
operating the liquid phase growth apparatus of Figs. 13
and 14. Symbol A represents motion of the wafer

cassette of the first batch. The wafer cassette of the
first batch is loaded into the loading chamber (L/C) 51
in first twenty minutes and then carried into the
hydrogen annealing chamber 52. In the hydrogen

5   annealing chamber 52, the temperature of the wafer
cassette 68 is raised for thirty minutes and hydrogen
annealing is implemented for ten minutes. The hydrogen
annealing is carried out at about 1040°C in the
hydrogen atmosphere. Immediately after the hydrogen

10   annealing, a small amount of SiH_4 (silane) may be
allowed to flow, so as to improve the surface property
of the porous Si layer 27. Then, the wafer cassette 68
is moved into the p⁻ type Si layer growth chamber 54 by
means of the horizontal conveying system 70 of the core

15   63 and the wafer cassette 68 is retained for ten
minutes before it is raised to the temperature of
growth. During this period, the solution 64a is cooled
to bring the p⁻ type Si into the supersaturated state in
the solution 64a. Before the wafer cassette 68 is

20   moved into the p⁻ type Si growth chamber 54, the
dissolving wafer cassette 86 holding p⁻ type Si wafers
is transferred from the Si source supply chamber 61
through the transport chamber 58 into the growth
chamber 54 and is immersed into the high-temperature

25   solvent to solve p⁻ type Si into the solvent. The
material of the solvent is, for example, In, Sn, or the
like. The solution containing p⁻ type Si is prepared in

this way.

Then, the wafer cassette 68 is immersed into the solution 64a by means of the vertical conveying system and the temperature of the solution 64a is slowly

5   reduced, whereupon the p⁻ type Si layer 25 is epitaxially grown on the surface of the porous Si layer 27. The period of time for this growth is about 30 minutes. After that, the wafer cassette 68 is lifted up from the solution 64a to the p⁻ type Si growth

10   chamber 54 and retained for ten minutes.

Likewise, the dissolving wafer cassette holding n⁺ type Si wafers is preliminarily immersed in the solvent to dissolve n⁺ type Si into the solvent for twenty minutes. The solution containing n⁺ type Si is prepared

15   in this way. Then, the wafer cassette 68 is immersed into the solution 64b and the temperature of the solution 64b is slowly reduced, whereupon the n⁺ type Si layer is epitaxially grown on the surface of the p⁻ type Si layer. The period of time for this growth is about

20   ten minutes.

After that, the wafer cassette 68 is lifted up from the solution 64b and moved into the unloading chamber 56. The wafer cassette 68 is cooled to room temperature in the unloading chamber 56 for fifty five

25   minutes. After that, the wafer cassette 68 is taken out of the liquid phase growth apparatus in last five minutes.

Symbol B represents motion of the wafer cassette
of the second batch. The wafer cassette of the second
batch is also moved according to the time chart of Fig.
15 and the motion thereof is similar to the motion of
the wafer cassette of the first batch. Therefore, the
description of the second batch is omitted herein. The
liquid phase growth apparatus of Embodiment 4 allows
the liquid phase growth of a new wafer cassette every
60 minutes.

In the liquid phase growth apparatus and liquid
phase growth methods, the cooling may be implemented by
liquid like water or liquid metal.

According to the liquid phase growth methods of
the present invention, the solution is cooled from the
interior thereof so as to suppress the temperature
difference between the interior and periphery of the
solution, which permits the growth in uniform
thickness. The growth material is dissolved into the
solvent to prepare the solution and the substrate is
immersed into the solution stored in the crucible
whereby the deposited film can be grown on the
substrate by the liquid phase growth from the solution.
When the central part of the solution is cooled in the
cooling section, the temperature difference is canceled
between the central part and peripheral part of the
solvent, whereby the growth in uniform thickness can be
implemented both in the central part and in the

peripheral part. The present invention also provides
the apparatus used in the foregoing methods.